Synthesis of Polyisobutylene with Carboxylic Chain End Functionality and Its Reactions

Ph. D. Theses

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I. Introduction and Aims

Polyisobutylene (PIB) is a hydrophobic, fully saturated linear macromolecule, which can be synthesized only by carbocationic polymerization of isobutylene. It has outstanding physical, chemical and biological properties. Low glass transition (-60 °C) and high decomposition (>300 °C) temperatures of PIB make it suitable for a wide range of applications where rubbery properties are preferable. Considering the above mentioned properties of PIB, it is an advantageous building material in many polymer systems. Due to its fully saturated hydrocarbon backbone, it has outstanding chemical resistance and stability. However, this property strongly limits the further modifications of PIB. Nowadays on the basis of the recent developments of polymer chemistry the synthesis of complex polymer architectures for special applications can be carried out. Specialty applications of polymers require well-defined structure and functionality. The success of direct, quantitative chain end functionalization of PIB obtained by quasiliving carbocationic polymerization of isobutylene has resulted in significant advances in both the chemistry and utilization of PIB. The successful syntheses of tertiary chloride, allyl, diphenyl-methoxy and 2-alkyl-furyl end groups are accessible by this method.

A simple and nearly quantitative process was developed in the course of my Ph.D. research in order to obtain polyisobutenyl carboxylic acid (PIB-COOH). The carboxyl group is one of the most valuable functional groups thanks to its reactivity and versatile derivatization possibilities. Moreover, PIB bearing carboxylic chain end can be a useful building block in different block-copolymer or network syntheses as well as starting material in further polymer analogous reactions. The aim of my research was to develop a process for the synthesis of PIB-COOH with quantitative chain end functionality. This route is based on the production of PIB with quantitative olefinic chain end and its subsequent ozonolysis, which leads to carboxylic chain end functionality by the decomposition of the double bond. I have examined the further modification of PIB-COOH by simple organic reactions in order to demonstrate the potential applications of this polymer.

II. Applied Methods

In the course of my experiments the synthesis of polyisobutylene with well-defined chain end functionality was carried out by quasiliving carbocationic polymerization of isobutylene in the presence of tertiary chloride initiator, $TiCl_4$ catalyst, and nucleophilic

additive in N_2 atmosphere at -78 °C. The "in-situ" quantitative terminal functionalization of PIBs by three different compounds, allyltrimethylsilane (ATMS), 1,1-diphenylethylene (DPE) and 2-methylfuran was carried out. These polymers served as a starting materials for my further experiments to obtain carboxyl group at the PIB chain end. The ozonolysis of these polymers was accomplished in a 10 w/w% solution. In order to optimize the ozonolysis reaction, different solvents, temperatures and reaction times were applied. The purification of polymer samples was performed by precipitation into methanol.

The further derivatization of PIB-COOH, synthesized by our method, was executed by Mitsunobu esterification, by amination after successful PIB acid chloride preparation and by reduction.

The surface activity of PIB-COOH was examined by UV-VIS spectroscopy in the case of *n*-hexane and water solvent mixture.

The "thiol-ene" type addition of allyl terminated PIB with thio carboxylic acids were also carried out.

The average molecular weight and molecular weight distributions of polymer samples were determined by size exclusion chromatography (SEC) and atmospheric pressure photo ionization mass spectrometry (APPI(-)-MS). The structure of the chain end of polymer samples was analyzed by ^{1}H NMR, FT IR spectroscopy and APPI(-)-MS as well.

III. New Scientific Results

1.

Quenching of isobutylene polymerization with methanol after the chain end functionalization with 1,1-diphenylethylene let to the formation of a product mixture with two different chain ends, i. e. 1,1-diphenylethyl and 1,1-diphenyl-1-metoxy end groups. For my further experiments, the relevant terminal olefinic chain end, i.e. 1,1-diphenylethyl end group was developed by a simple method. The formation of 1,1-diphenylethyl terminated polyisobutylene was carried out after the polymerization and "in-situ" functionalization reaction without separation of the product. The success of this method based on the fact that HCl, generated in the reaction of the catalyst and methanol catalyses the elimination of the methyl ether group, while 1,1-diphenylethyl terminated polyisobutylene is formed. This process quantitatively and reproducibly results in 1,1-diphenylethyl terminal PIBs.

2.

I have found that the ozonolysis of allyl terminated PIB leads to the formation of a polymer with stable ozonide end group. The decomposition of this terminal ozonide was achieved by heat treatment leading to carboxylic end functional PIB. The development of PIB-COOH was proven by the results of ^{1}H NMR and APPI(-)-MS analyses.

3.

In the course of my studies on the effect of solvents, temperature and reaction time on the ozonolysis reaction, I have concluded that the reaction between ozone and double bonds takes place instantly, and the ozone results in the quantitative transformation of olefinic bonds. The structure of the products after ozonolysis carried out in n-hexane, dichloromethane or toluene did not show considerable differences.

4.

The ozonolysis of 1,1-diphenylethyl terminated PIB directly led to the decay of the olefinic bond and carboxylic chain end formation was observed. This transformation was verified by the results of ^{1}H NMR, FT IR and APPI(-)-MS analyses.

5.

The functionalization of PIB with 2-methylfuran does not lead to olefinic chain end directly, but to furyl group. Before performing ozonolysis, the formation of double bond at the polymer chain end was obtained by opening the furan ring. The analysis after ozonolysis showed the presence of neither furan nor olefin functional polyisobutylenes. The APPI(-)-MS measurement showed carboxylic end group formation.

6.

Allyl terminated PIB was reacted with 3-mercapto propionic acid in the presence of a radical initiator (2,2′-azobis(2-methylpropionitrile)). According to the results of ^{1}H NMR analysis, the “thiol-ene” reaction took place successfully, and yielded carboxylic functional PIB.

7.

The successful realization of esterification of PIB-COOH was done by two different alcohols. Mitsunobu esterification with methanol and ethanol resulted in PIB-methyl ester and PIB-ethyl ester, respectively, according to the ^{1}H NMR analysis of the products.

8.

The reaction between PIB-COOH and thionyl chloride resulted in the synthesis of polyisobutenyl acid chloride (PIB-COCl). Precipitation of this PIB-COCl into methanol led to direct methyl ester formation. The addition of 2-hydroxyethyl methacrylate to bifunctional PIB-COCl yielded a polymer with methacrylate end groups. This is a simple and quick method to obtain PIB macromonomer, which can be further polymerized, for example, by radical polymerization.

9.

The reaction between PIB-COCl and propylamine quantitatively resulted in the transformation of the PIB chain end. According to the analysis of the product of this reaction, a PIB with amide bonded chain end was formed.

10.

Examining the reduction of PIB-COOH with $LiAlH_4$, complete transformation by this reaction was obtained only after long reaction time. As a result of this reaction, PIB with hydroxyl end group formed.

11.

For the possible application of PIB-COOH in oil additive formulations, a test on the miscibility of *n*-hexane and water was performed. Indicator containing water was shaken with n-hexane with or without PIB-COOH. UV-VIS spectrometric analysis was done on the separated organic phase. This experiment showed that the polyisobutylene bearing polar end group behaves as surfactant in the case of the tested *n*-hexane-water solvent mixture.

IV. Significance of the New Results

During my Ph. D. studies, the synthesis of PIB with carboxylic functional group has been successfully carried out with a simple and nearly quantitative process. The PIB-COOH could be used as starting material in the production of PIB based oil additives. Our method is based on the ozonolysis of PIBs containing terminal unsaturation. Three different compounds, allyltrimethylsilane, 1,1-diphenylethylene and 2-methylfuran were used in the course of quasiliving carbocationic polymerization of isobutylene in order to develop the appropriate polymer chain end structure by complete addition to the polymer chain end. Ozonolysis of all

these functionalized PIBs showed carboxylic acid end group formation. The ozonolysis of allyl terminated PIB (PIB-Allyl) resulted in the formation of an intermediate stable ozonide product. Decomposition of this ozonide induced by heat treatment in toluene led to PIB-COOH. This process and the PIB-COOH product obtained thereby have gained patent protection worldwide [1]. The modification of PIB-Allyl by "thiol-ene" reaction was also examined. The formation of PIB-COOH proved to be successful in the "thiol-ene" reaction with 3-mercaptopropionic acid.

Further reactions of PIB-COOH were also demonstrated by esterification, amination and reduction. These findings with PIB-COOH can open new fields in the application of this chemically inert and biocompatible polymer. The surfactant property of PIB-COOH was demonstrated with the mixture of *n*-hexane and water solvents. This experiment indicates the applicability of PIB-COOH in oil additives.

V. Publications and Presentations

Publications

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